Electronic Structure of Benzo[3,4]cyclobuta[1,2]cycloheptenyl Ions: The Aromaticity–Tropicity Dilemma

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An ^{1}H and ^{13}C NMR study of the benzo[3,4]cyclobuta[1,2]cycloheptenyl cation and anion has been undertaken in order to unravel the electronic structure of these species. The formal addition of two electrons to the cation can be seen as a conversion of a slightly diatropic and aromatic cation into an unstable, highly diatropic but antiaromatic anion. Self-consistent iterative Hückel, MNDO, and AM1 as well as graph-theoretical ring current calculations were carried out in order to clarify this confusion. Comparisons to the isoelectronic biphenylene and biphenylene dianion are especially revealing.

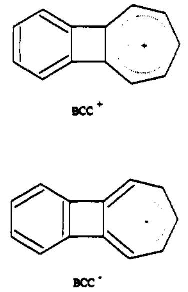
The relation between aromaticity and ring currents is perhaps one of the most intriguing and long-lasting problems in physical organic chemistry. Although the whole field has undergone some convergence during the last decade, there are still many questions to be answered.[2] Two important contributions have been given separately by Aihara[3] and Haddon,[4] who, although from different standpoints, derived analytical expressions between resonance energies and "ring current" intensities. For monocyclic annulenes an almost perfect relation was found between London susceptibility (χ_π) and aromaticity as defined by Dewar resonance energy (RE). The situation is more complicated for polycyclic systems, but the overall London susceptibility is said to be a more reliable criterion for aromaticity than the ring current intensities of a given system.[5]

$$\chi_\pi = -\sum \mathrm{RE}^{(i)}\Phi_i^2$$

For systems of this kind it was shown that the *i*th ring resonance energy was related to the *i*th ring susceptibility and that the two properties only differed by a weighting factor Φ^2 which is proportional to the corresponding ring area squared.[3] In polycyclic systems,[3c] however, the sign of the overall resonance energy does not always differ from the sign of the overall susceptibility; i.e., a compound may be diatropic but antiaromatic according to this expression.

Larger rings will give larger contributions to the susceptibility than to the resonance energy. Consequently, the sign of the overall susceptibility is in many cases determined by one or two large subcircuits with small ring resonance energies. It could be shown that if the signs of these ring resonance energies are different from the overall resonance energy then the sign of the overall susceptibility will be the same as that of the overall resonance energy.[3c] Hence, one should for some fused 4n-systems be able to verify that a negative resonance energy is connected to a negative overall susceptibility, i.e., diatropicity. The heptalene dianion and bicyclo[6.2.0]decapentaene are two systems of this kind which by this graph-theoretical version of the London theory have been claimed to be diatropic but antiaromatic (negative RE) in nature.[3d] Systems which have some important contributions from 4n rings are especially interesting to study, but unfortunately the London susceptibility, which is a calculated property, is in these types of systems quite sensitive to the actual method of calculation, i.e., the kind of wave functions that are used. There are several excellent reviews dealing with the diagnosis of aromaticity from ring currents, and we would especially recommend that by Mallion.[2a]

Chart I


BCC$^+$

BCC$^-$

The aromaticity–antiaromaticity topic has earlier been addressed in studies of benzo[3,4]cyclobuta[1,2]cycloheptenyl (BCC) ions.[6] Staley claimed, mainly based on proton shifts of the six-membered ring ($\Delta\delta < 0.7$ ppm) of the two ions, that the anion behaved both as a local 4n-π and a peripheral 4n + 2π-electron system.[6a] By adding two electrons to the LUMO of the BCC cation, the proton NMR shifts could be interpreted as if the peripheral 4n paramagnetic ring current was quenched by a peripheral diamagnetic ring current. Small shift changes, however, are difficult to interpret safely due to ion pair effects, etc. Lombardo and Wege,[6b] who first prepared the cation, argued on the basis of proton data that the cation structure was best described as consisting of two independent 6π systems. Such structures have gained support from considerations of bond orders as calculated by MNDO.[7] From the induced carbon NMR shifts relative to the heptatriene precursor one also concluded, that the charge was located mainly in the seven-membered ring for both

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[2] (a) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541. (b) *Aromaticity*; Garratt, P. J., Ed.; John Wiley and Sons: New York, 1986. (c) Haigh, C. W.; Mallion, R. B. *Prog. NMR Spectrosc.* **1980**, *13*, 303.

[3] (a) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 5913. (b) Aihara, J. *J. Am. Chem. Soc.* **1985**, *107*, 298. (c) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115. (d) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 5704.

[4] Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

[5] Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1980**, *46*, 719.

[6] (a) Staley, S. W.; Heinrich, F.; Orvedahl, A. W. *J. Am. Chem. Soc.* **1976**, *98*, 2681. (b) Lombardo, L.; Wege, D. *Aust. J. Chem.* **1978**, *31*, 1569. (c) Lombardo, L.; Wege, D. *Tetrahedron Lett.* **1972**, *48*, 4859.

[7] (a) Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455. (b) Glidewell, C.; Lloyd, D. *J. Chem. Educ.* **1986**, *63*, 306.

0022-3263/93/1958-2020$04.00/0

ions.[6b] However, any shift comparisons to model systems must be handled cautiously especially if the tropicity of the two compared systems varies.[8] Lombardo et al.[6b] argue that the carbon shift changes of the seven-membered ring going from BCC to BCC$^+$ are the same as when going from cycloheptatriene to the tropylium ion (29.5 ppm). This observation supports that the positive charge is located to the seven-membered ring. However, this statement is only valid if the two systems respond to charge in a similar way. If BCC$^+$ is less diatropic than the tropylium cation, one would for BCC$^+$ expect the total downfield shift of the seven-membered ring carbons to be larger, since shielding anisotropies on carbons also must be taken into account and added to the charge induced shifts.[8]

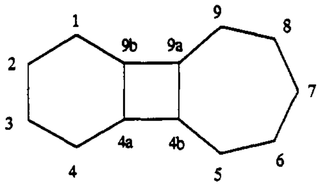
The MNDO calculations[7] pointed to some inherent limitations of discussing only a few protons shifts of these structures. For the C_{2v} structures, a fairily strong bond fixation was suggested in the benzenoid rings for both ions. But the C_{2v} structure for the anion was slightly higher in energy than the C_s structure, where delocalization is obvious in the benzenoid ring while bond fixation is noted in the larger ring, i.e., quite opposite to the bonding situation in the C_{2v} structure. The increase in diatropicity in the anion relative to the cation can thus be explained by the extensive delocalization found in the benzenoid rings of the equilibrating C_s structures.

In this study we offer completely assigned ^{1}H and ^{13}C NMR shifts of the BCC ions. The experimental study is complemented with semiempirical MO calculations and also a graph-theoretical study following Aihara's formalism[3] in order to assess the ring current situation. Comparisons will be made to isoelectronic biphenylene (BP) and its dianion, which should have many of the mentioned properties in common.

Results and Discussion

NMR Spectroscopy. In an earlier report on the ions of BCC[6a], it was noted that a small net *downfield* shift of the six-membered ring protons occurred by a two-electron reduction. If the expected shielding due to charge is accounted for via the common K_H = 10.7 ppm/electron, this observation indicated that the "tropicity" measured at these positions increased by more than 1 ppm in this reduction process. We could confirm this conclusion by adding the calculated charge-induced protons shifts, using a self-consistent interactive Hückel method, to the observed shifts of the BCC cation. The difference between the observed proton shifts for the BCC anion and these charge-corrected shifts will constitute the "tropic" shifts indicated by this formal two-electron transfer. These diatropic shifts are 1.40 and 1.30 ppm for the benzene H1 and H2 positions, while H5, H6, and H7 are shielded by −0.90, −0.75, and −0.92 ppm, respectively. Hence, the suggestion by Staley could prevail,[6a] i.e., that the paratropic subcircuit of the cycloheptatrienyl anion part to a large extent is quenched by the diatropic peripheral circuit.

Table I. ^{1}H and ^{13}C NMR Chemical Shifts of BCC$^+$ and BCC$^-$



	BCC$^+$		BCC$^-$		BCC$^-$ − BCC$^+$	
position	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$	$\Delta\delta(^1H)$	$\Delta\delta(^{13}C)$
1	7.21	126.8	7.64	115.6	+0.43	−11.2
2	7.25	138.5	7.03	114.8	−0.22	−23.7
4a		151.4		126.3		−25.1
4b		182.3		122.0		−60.3
5	7.58	136.2	6.26	121.2	−1.32	−15.0
6	8.19	163.3	4.09	95.3	−4.10	−68.0
7	7.67	143.2	5.56	132.5	−2.11	−10.7

If one compares the NMR shift changes of the BCC ions (Table I) with the shifts induced by the corresponding two-electron reduction of biphenylene,[9] several interesting observations can be made. A reduction of the neutral BP to the dianion causes upfield changes of the C 2,3 carbons of approximately −32 ppm, while the corresponding H 2,3 protons are shielded by −1.2 ppm, i.e., a smaller proton upfield shift than would be expected based on the shift/charge correlations for proton and carbon. The general conclusion of this study was that BP^{2-} is more diatropic than the parent BP, a claim that also was supported by experimental bond orders (the *Q*-method, see below).[10] In BCC, the corresponding carbon shift difference of ca. −24 ppm is accompanied by a proton shielding of only −0.2 ppm at these 2,3 positions. In fact, in BCC, the C 1,4 carbon shift change ($\Delta\delta$ = −11.4) has a different sign from that of the corresponding protons ($\Delta\delta$ = +0.4). From the proton data, therefore, it is tempting to assume that the peripheral subcircuits are more important for the BCC ions than the corresponding isoelectronic BP systems, thus causing BCC$^+$ to be less diatropic and the BCC$^-$ more diatropic than BP and BP^{2-} systems, respectively. This is also manifested in the ring current calculations (vide infra). A similar discussion can be held by the comparison with the NMR data from the corresponding benzocycloheptatriene conversion from cation to anion.[11] Although consistent with the previous views,[6a] all the observed differences in proton shieldings are quite small and difficult to assign to ring current effects only. Just a few positions are actually studied and ion pairing effects on the proton shifts can be of a significant magnitude.

When it concerns charge induced chemical shifts in delocalized systems, the most used empirical relationship is a total charge-induced carbon shift of approximately 160 ppm per added electron.[12] As an example, if the tropylium ion is formally transferred by four electrons into the cycloheptatrienyl trianion, a system of similar tropicity as the tropylium cation, a shift/charge factor K_C of 157 ppm/e is derived.[13] In earlier reports on ^{13}C induced shifts of ions of delocalized hydrocarbons, it was noted that reduction to more paratropic (or less diatropic) species was accompanied by a lower than expected shift/charge factor, $K_C < 160$ ppm/e.[8] To exemplify, when the diatropic benztropylium cation is reduced to the paratropic anion, we could observe a K_C of only 89 ppm/e.[11] Consequently, reduction to more diatropic species gave K_C larger than

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[8] (a) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937. (b) Eliasson, B.; Johnels, D., Edlund, U.; Müllen, K. *Ibid.* **1990**, 897.

[9] Benken, R.; Finneiser, K.; von Puttkamer, H.; Günther, H.; Eliasson, B.; Edlund, U. *Helv. Chim. Acta* **1986**, *69*, 955.

[10] Günther, H.; Shyoukh, A.; Cremer, D.; Frisch, K.-H. *Liebigs Ann. Chem.* **1978**, 150.

[11] Sethson, I.; Johnels, D.; Edlund, U. *Acta Chem. Scand.* **1990**, *44*, 1029.

[12] Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

[13] Bahl, J. J.; Bates, R. B.; Beavers, W. A.; Launer, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 6126.

Table II. Calculated π-Charges of BCC Ions Using Iterative Hückel, MNDO, and Charge-Induced ^{13}C NMR Chemical Shifts

	BCC^- π-charges		BCC^+ π-charges		Δπ		
	MNDO	β,ω',ω''	MNDO	β,ω',ω''	MNDO	β,ω',ω''	$\Delta\pi_{exp}$
C1	−0.063	−0.014	+0.108	+0.077	−0.171	−0.091	−0.054
C2	−0.073	−0.097	+0.052	+0.045	−0.125	−0.142	−0.113
C4a	+0.025	−0.097	−0.093	−0.030	+0.118	−0.067	−0.120
C4b	−0.189	−0.100	+0.172	+0.140	−0.361	−0.240	−0.289
C5	+0.094	−0.005	+0.034	+0.087	+0.060	−0.092	−0.072
C6	−0.355	−0.177	+0.217	+0.136	−0.572	−0.313	−0.325
C7	+0.120	−0.016	+0.020	+0.095	+0.100	−0.111	−0.051

160 ppm/e. The two-electron reduction from BP to the more diatropic BP^{2-} thus afforded a K_C of 178 ppm/e.[9] In the two-electron reduction of BCC, we observe a shift/charge factor of 209 ppm/e on going to the anion. This is in nice agreement with the proposal of tropicity based on the proton data and means that the BCC^- is more diatropic than the corresponding cation, a statement, which, as will be shown later, contradicts the expectations based on Dewar resonance energies (RE), according to which BCC^- is antiaromatic and the BCC^+ aromatic.

Addition of a more efficient cation-solvating medium, like *N,N'*-dimethyl-*N,N'*-ethyleneurea (DMEU), to the tetrahydrofuran (THF) solution of the anion did not significantly change the induced carbon shifts of the anion. This observation is consistent with a solvent separated ion pair (ssip) structure in both solvent systems, where there is an excessive delocalization of charge into the benzene part. A delocalized carbanion will favor solvent-separated structures relative to a more localized system. As an example, the delocalized fluorenyllithium species, isoelectronic to the BCC anion, is mainly ssip in THF, while indenyllithium mainly exists as contact ion pair under this solvent condition.[14]

In diethyl ether (DEE), known to exclusively favor contact ion pairs (cip), the only significant spectral difference is a slight shielding of the H-6,8 protons (−0.2 ppm) as well as the corresponding carbon shift differences of the 6,8-positions being −6.9 ppm. From the proton shifts, there is no indication of a change in "tropicity" going to more intimate ion pairs, such as an increased contribution from the paratropic seven-membered subcircuit.

MO and Graph Theoretical Calculations. In Table II we have listed the π-electron densities calculated using both MNDO and a self-consistent iteractive β,ω',ω'' Hückel method. Wilcox has claimed the latter to be the best MO method for biphenyloid hydrocarbons.[15] However, in the present ions, the only significant change relative to simple Hückel calculations is a slightly decreased charge alternation in the anion system.[6a] The gross pattern of calculated charges, whether using MNDO or Hückel, is largely in agreement with the ^1H and ^{13}C NMR data reported in Table I. The C-6,8 positions and the quaternary C-4b,9a positions seem to accomodate most of the charge for both ions, followed by the C-2,3 positions in the anion but the C-1,4 positions in the cation. Charge alternation is more obvious using MNDO, especially so for the anion. Using the mentioned K_C of 209 ppm/e, experimental π-charge changes ($\Delta\pi_{exp}$) can be derived, and compared with the calculated ones. From Table II, it is seen that the Hückel-derived charges better correspond to the experimental ones. The reported $J_{1,2}$ and $J_{2,3}$ couplings for BCC^- being 8.00 and 7.06 Hz also better correlate to the bond orders given by the Hückel calculation. These couplings are also close to those found for the BP ion (cf. BP^{2-}; $J_{1,2} = 7.74$ Hz and $J_{2,3} = 6.05$ Hz) but contrast with the bond fixation in the parent biphenylene ($J_{1,2} = 6.87$ Hz and $J_{2,3} = 8.34$ Hz). The discrepancy between the two methods of calculation is most obvious for the BCC anion.

Another approach to illustrate the π-electron structure of the two ions is to use the *Q*-value method by Günther.[10] The *Q*-values, defined as the ratio between the $P_{1,2}$ and the $P_{2,3}$ bond orders, are 1.40 for BCC^- and 0.82 for the BCC^+ using the Hückel-derived bond orders. According to this empirical method, benzoannulenes of this size could be classified into three categories depending on the characterization of the π-system annelated to the benzene ring: (i) delocalized (4n + 2)-annulenes if *Q*-values > 1.10, (ii) delocalized 4n-annulenes if *Q*-values < 1.04, and (iii) systems without any cyclic delocalization if *Q*-values are in between these two values. The experimentally found *Q*-values, which is based on the scalar couplings above, is 1.20 for BCC^- if corrected for strain effects.[9] These results are quite similar to those reported for the BP ions;[9] i.e., BCC^- can be classified as a 4n + 2 π delocalized system, while BCC^+ can be treated as a partly paratropic or at least less diatropic system.

According to our MNDO calculations, and as also have been reported earlier,[7] the cation of BCC optimizes to a C_{2v} symmetric structure. The anion on the contrary, gives a C_s structure as the global minimum, which is 0.5 kcal/mol more stable than the C_{2v} structure if BCC^- is treated as a free anion. This difference increases to 1 kcal/mol if a counterion is included and treated as a sparkle. Using AM1 calculations, the energy difference vanishes for the free ion but the C_s structure is still 1 kcal/mol more stable, if the counterion is included. Such small energy differences, however, are dangerous to give any significance. Ion-pairing effects present in carbanion systems, but of minor concern for carbocations, are hard to account for. It is also well established that MNDO methods underestimate conjugation in comparison to Hückel methods.[16]

This latter condition is also the reason why earlier MNDO structural studies of BCC ions have shown that the ions should be considered as structures where the ionic seven-membered ring is connected to the 4n + 2π benzene ring by two bonds of low bond order.[7] In other words, "there is no delocalization across the four-membered rings". The NMR results presented above are not consistent with such a view, since more than 0.5 electron ($\Delta\pi_{exp}$) enters into the benzene part going from the cation to the anion.

A theoretical estimate of the resonance energies, ring currents and magnetic susceptibilities can be made for

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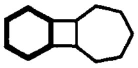
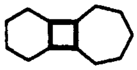
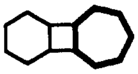
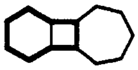
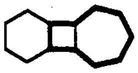
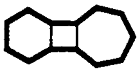
[14] (a) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (b) Chan, L. L.; Smid, J. *J. Am. Chem. Soc.* **1968**, *90*, 4654. (c) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661. (d) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (e) Lejon, T.; Edlund, U.; *Acta Chem. Scand.* **1989**, *43*, 275.

[15] Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1983**, *105*, 7191.

[16] Sethson, I., Johnels, D.; Lejon, T.; Edlund, U.; Winds, B.; Sygula, A.; Rabideau, P. W. *J. Chem. Soc.* **1992**, *114*, 953.

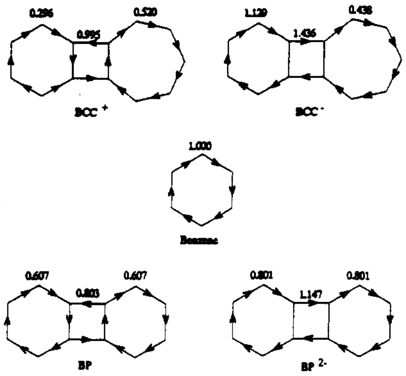
Table III. Ring Current Calculations Using a Graph-Theoretical Method

	BCC$^+$			BCC$^-$		
	circuit suscept, χ_0	circuit currents, I_0	circuit RE, β	circuit suscept, χ_0	circuit currents, I_0	circuit RE, β
	+0.996	+0.996	+0.221	+0.278	+0.278	+0.062
	−0.055	−0.143	−0.083	−0.089	−0.230	−0.133
	+1.698	+1.214	+0.193	−2.306	−1.649	−0.262
	−0.219	−0.158	−0.025	−0.582	−0.420	−0.067
	−0.271	−0.152	−0.019	+1.454	+0.815	+0.102
	−1.509	−0.542	−0.043	+3.538	+1.271	+0.101

London susceptibility = $0.641\chi_0$
approx resonance energy = 0.244β

London susceptibility = $2.294\chi_0$
approx resonance energy = -0.198β

Scheme I. Positive and Negative Bond Currents (Drawn Clockwise and Counterclockwise, Respectively)



the ions of BCC as well as for the individual subcircuits using Aihara's graph-theoretical approach[3] and in conjunction with the iterative Hückel MO method. The resulting data for both ions are shown in Scheme I and Table III. If we consider the BCC cation to start with, it can be noticed that the overall London susceptibility is significantly lower than for benzene ($0.641\chi_0$ compared with the susceptibility of benzene = χ_0). From the circuit susceptibilities (Table III), one can identify the main reasons for that. The largest subcircuit which gives a paratropic contribution outweighs the diatropic contribution from the "tropylium" subcircuit. However, the RE of this peripheral circuit is minor, and we are left with an overall structure with high positive resonance energy but a reduced diatropicity. Alternatively, this could also be seen in the bond current flow as depicted in Scheme I.

In the anion, on the other hand, the overall London susceptibility is much larger, which stems from the fact that the susceptibilities are dominated by the diatropic contributions from the largest subcircuits.[17] The circuit resonance energies, however, are independent of circuit areas, and the total RE is therefore dominated by the smaller "antiaromatic" circuit RE. The final result is a strongly diatropic structure which is "antiaromatic" in nature according to the negative RE. The bond current flow is also quite different compared to that of the cation, and the increased diatropic behavior especially for the benzene ring protons is clearly visualized. The addition of two electrons to the LUMO of the cation then transforms a weakly diatropic but aromatic cation into a strongly diatropic but "antiaromatic" anion, according to these calculations. This is exactly what the NMR data tell us. It is also consistent with other experimental findings. The cation is quite stable; in fact, it has earlier been isolated for elementary analysis.[6b] The diatropic anion, however, is quite unstable unless at low temperature and is prone to undergo rearrangement to the fluorenyl anion.[6a]

The coexistence of diatropicity and antiaromaticity in a single system has earlier been claimed theoretically. The present report is the first experimental support for this view by comparing similar structures (circuit areas) with different electronic configuration.

It is of course of interest to compare these results with the corresponding calculations for the BP ions. Both BP^{2+} and BP^{2-} have identical ring currents and energies, and this is why a comparison of the neutral biphenylene to only one of the ions is of interest. The bond currents for the neutral system, as earlier reported,[3c] and for the dianion are shown in Scheme I. The London susceptibility of BP is 0.90, i.e., close to benzene, and this structure also has a large positive overall RE (0.318β). The dianion, however, is even more diatropic ($\chi_\pi = 2.04$), but the RE energy is negative ($-2.126\ \beta$). We have earlier noted an increased diatropicity of the dianion as well as of the dication relative to the neutral precursor. Vogler also reported in a π-SCF force field calculation of ring currents in BP and its dianion that the diamagnetic ring current is larger for the proton shifts in the dianion.[18] The similarities to the BCC systems are thus quite striking. We also observe an instability of

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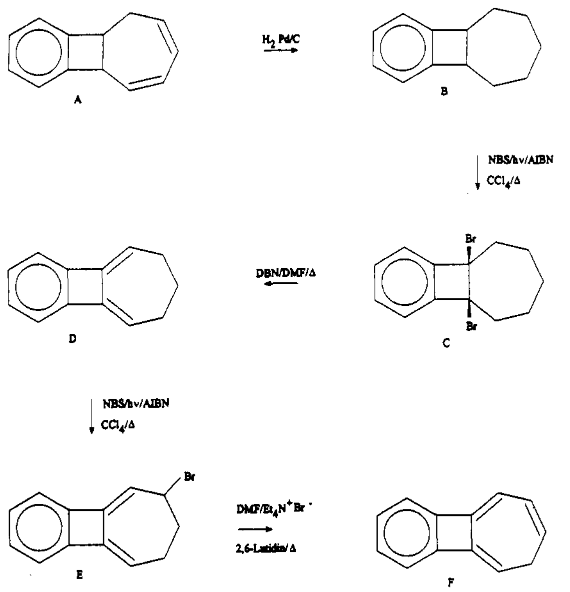
[17] Bond currents in BCC anion have earlier been reported in a review article, Staley, S. W. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; p 33. Although the relative order of bond currents for the subcircuits is the same, substantial deviations can be noted from those reported herein. This discrepancy is explained by the sensitivity of these calculations to what kind of wave functions are used.[2a]

[18] Vogler, H. *Magn. Reson. Chem.* **1985**, *23*, 1040.

Scheme II



the BP dianion, since a ring-opening occurs of the dilithium salt yielding 2,2′-dilithiobiphenyl.

Conclusion

To conclude, by formally adding two electrons to the BCC cation, the gathered NMR and theoretical data are best explained as if the slightly diatropic but aromatic cation of BCC is transferred to an unstable, highly diatropic but "antiaromatic" anion.

Experimental Section

Synthesis. The preparation of 4b,9a-dihydro-5H-BCC (A) (Scheme II) was based on the methods presented by Lombardo and Wege[6b,c] and Hahn and Johnson,[19] where the benzyne–cycloheptatriene reaction was performed in dichloroethane. Removal of the undesired 7-phenylcycloheptatriene from the product mixture was done using tetracyanoethylene. The final purification of A was brought about by column chromatography (CCl_4/silica gel) followed by vacuum distillation necessiated to remove a trace of CCl_4 which partly inhibits the following hydrogenation.

The cis-5,6,7,8,9,9a-hexahydro-4bH-BCC (B) was obtained by catalytic hydrogenation in a Parr apparatus (10% Pd on carbon, ca. 14 mg/g diene;methanol, 11–13 mL/g diene) with an initial pressure of ca. 60 psi. The reduction of the diene system was completed in ca. 3 h at ambient temperature. The system showed no apparent tendency to over-reduction leading to any saturation of the benzo ring.

Distillation gave colorless oil which crystallized spontaneously on standing. ^{13}C-NMR ($CDCl_3$/TMS): $\delta = 28.5, 30.4, 48.5, 121.9, 126.9$, and 148.0.

The remaining steps, i.e., the consequtive syntheses of 4b,9a-dibromo-5,6,7,8,9,9a-hexahydro-4b*H*-BCC (C), 7,8-dihydro-6H-BCC (D), 6-bromo-7,8-dihydro-BCC (E), and the end product 6*H*-BCC (F), were performed essentially as has already been described and in similar yields. The last transformation to F was done according to method B as described earlier.[6b] The triene was purified using the so-called minimum effort liquid chromatography (MELC).[20] The silica gel column (Merck, 60 cm) was eluted with cyclohexane and fractions checked for triene (F) content using TLC. Fractions giving a single triene spot were pooled, and the solvent was removed by careful evaporation.

The purity of the triene and the intermediate products (A–E) was checked using NMR spectroscopy in relation to earlier published shift data. The overall synthetic route was repeated three times, and the average yields for various steps were close to those earlier reported.

NMR Measurements. The BCC cation was prepared by adding 30 mg of triene F in 0.5 mL of dry CH_2Cl_2 to 1 mL of a CH_2Cl_2 solution of 68 mg of trityl perchlorate at −60 °C. The reaction mixture was allowed to warm to room temperature, and the resulting solid was centrifuged. The supernatant was removed with a double-ended needle, and the crystals were dried in vacuo at room temperature. The crystals were subsequently dissolved in 0.7 mL of acetonitrile-d_6 to give a deep red solution. The resulting ^{1}H NMR spectrum, recorded at room temperature, corresponded to that reported earlier.[6b,c]

The anion was generated directly in the NMR tube by adding 1.5 equiv of concentrated n-BuLi (9 M in hexane) to a degassed, cooled ether solution of triene F. The NMR tubes were evacuated and sealed off from the vacuum line. The THF/DMEU (5:1) samples were prepared by addition of degassed DMEU from a side-arm on the tube. The low-temperature spectra were obtained at −40 °C.

The NMR measurements were performed on Bruker AC-P 250 and AM 500 spectrometers. The chemical shifts were measured relative to cyclohexane and adapted to the δ scale with δ (^{1}H cyclohexane) = 1.43 ppm and δ (^{13}C cyclohexane) = 27.70 ppm.

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